

⁴¹K AND ²⁶Mg IN ALLENDE INCLUSIONS AND A HINT OF ⁴¹Ca IN THE EARLY SOLAR SYSTEM. J.C. Huneke, J.T. Armstrong and G.J. Wasserburg, Panurge Wing of the Lunatic Asylum, Div. Geol. Planet. Sci., Caltech, Pasadena, CA 91125

²⁶Mg* from ²⁶Al decay in primitive inclusions in meteorites requires the injection into the proto-solar nebula of stellar material freshly processed within a few m.y. of inclusion formation [1]. Demonstration of the presence of other short-lived nuclei with $\tau_{1/2} \ll 1$ m.y. would give further evidence for the injection event and place strong constraints on both the time scale and the process. Our efforts were directed toward measuring the isotopic composition of Mg and K in Ca-Al-rich Allende inclusions using an ion microprobe with high mass resolving power RP (Panurge, a CAMECA IMS-3F instrument). ⁴¹Ca ($\tau_{1/2} = 1.0 \times 10^5$ y) which decays to ⁴¹K is an excellent candidate for such studies, as the refractory Type B inclusions in Allende have a high Ca content and extremely low K content. This problem was first addressed by Begemann and Stegmann [2], after D. Clayton proposed [3] that extinct radioactivities were incorporated into refractory grains in the immediate environment of a presolar stellar source and that the decay of the parent nucleus had taken place prior to solar system formation. They reported a normal K composition in an Allende inclusion with the limit $^{41}\text{K}^*/^{40}\text{Ca} \lesssim 10^{-5}$.

Ion microprobe analysis avoids contamination from separation chemistry and permits analysis of small volumes of matter carefully selected for purity, and sputter ion yields of alkali and alkaline earth elements are high. These considerations favor ion microprobe analysis for trace K and Mg isotopic measurement. K and Mg isotopic compositions were measured on inclusion WA which was known to have ²⁶Mg* and HAL which has no ²⁶Mg*. As isobaric interference from molecular and multiply charged ions may cause serious difficulties, the work for K was done at RP4500 and for Mg at RP2500. Selected grains were mounted, polished, and gold coated. A primary O⁻ ion beam at 15 kV was used for sputtering with 3-12 nA ion current focussed into a 10-30 μ area. Ion transfer optics were adjusted to maximize the useful yield of ions sputtered from a 25 μ area of sample surface. An aperture further limited the transmitted beam to ions sputtered from the central 10 μ area. The primary beam was rastered 35 μ^2 to remove the coating from the area to be analyzed. High K⁺ and Mg⁺ intensities due to surface contamination were observed during the initial stages of sputter cleaning, which was continued until constant K⁺ currents were observed.

Mass spectra for Mg are shown in Fig. 1 at RP2700 and 4500. Peak widths at RP2700 are 7 mamu (10^{-3} amu) with peak maxima 3 mamu wide (>99%). The only notable interferences are ⁴⁸Ca⁺⁺ and MgH⁺. Doubly charged ions of Fe-region elements are significantly lighter than Mg, but multiply charged ions of most elements and molecules made of lighter elements are heavier. Contributions of ⁴⁸Ca⁺⁺ to mass 24 are substantial and if not eliminated yield large apparent ²⁶Mg⁺ through mass fractionation correction. ²⁴MgH⁺ ions at mass 25 are insignificant and there are no resolved interferences with ²⁶Mg⁺. Mg⁺ isotopic data were acquired by first automatically locating all peak maxima and then stepping the magnet field repetitively to peak sides to confirm peak location and to peak tops to acquire data. Errors are 2 σ of the mean of 10 ratio measurements and are the same as 2 σ calculated from total ion counts. The measurement on WA spinel yielded Mg identical in composition to terrestrial Mg. Mg in WA plagioclase gave normal ²⁵Mg⁺/²⁴Mg⁺ but 22% greater ²⁶Mg⁺/²⁴Mg⁺, confirming previous observations of very large ²⁶Mg excesses in WA [4,5]. Microscopic concentrations of Mg were apparent in the Mg⁺ ion image of the sample surface, resulting in large positive fluctuations in Mg⁺/Ca⁺ as the surface eroded. ²⁶Mg⁺/²⁴Mg⁺ trended to normal during these fluctuations, showing the particles are not enhanced in ²⁶Mg* from trapped Al₂O₃ grains with extinct ²⁶Al.

The mass 41 region for WA pyroxene is shown in Fig. 2 plotting ion cur-

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rent vs. mass. The field scan is regular, with no significant field reversals yielding apparent mass peaks. The lightest mass peak appears within 2 mamu of the expected position of ^{41}K determined relative to ^{40}CaH from known mass dispersion. The markers are positioned on $^{40}\text{CaH}^+$ with the mass differences calculated from the known nuclear masses. The correspondence of mass peaks to the calculated position supports their identification. All mass peaks at 39,40,41 and 42 within ± 30 mamu of K and Ca have been identified with the exception of a troublesome small interference 8 mamu larger than $^{42}\text{Ca}^+$ in the mass spectra of plagioclase and pyroxene. $^{39}\text{K}^+$ determined from an equivalent scan of mass 39 is shown in Fig.2 compared to $^{41}\text{K}^+$; the ratio $^{41}\text{K}^+ / ^{39}\text{K}^+$ is ten times greater than normal. A primary concern is whether ions identified as ^{41}K include ions of unrecognized species or reflected ions of abundant neighboring isotopes. The correspondence of the peak mass to the mass of ^{41}K within ~ 2 mamu is a strong argument that the detected ions are ^{41}K . Molecules made of lighter elements with lower binding energy are heavier than ^{41}K and are resolved. Combinations yielding heavier molecules are numerous and ions of the form $(\text{AB} \dots)^{n+}$ are a concern. A possible interference not yet evaluated is $^{50}\text{TiO}_2$ which is 6 mamu heavier than ^{41}K . Absence of effects in HAL hibonite and WA spinel show the ^{41}K excesses are not scattered ions of Mg, Al or Ca or related molecules. Similar demonstrations for Si and Ti will be done. Scattered ions would have to appear at high RP within 2 mamu of ^{41}K , which is unlikely but possible.

Data acquisition for $^{41}\text{K}^+ / ^{39}\text{K}^+$ was carried out as follows: (1) The relationship between magnetic field and voltage output of the Hall probe monitoring the field was determined at mass 41. (2) The difference in field between the $^{41}\text{K}^+$ peak, the $^{40}\text{CaH}^+$ peak and the intensity minimum between $^{40}\text{CaH}^+$ and $^{25}\text{MgO}^+$ was determined from mass spectra in which all ions were definitely present. The differences were reproducible to ± 0.5 mamu and correspond to values from mass spectrometer dispersion. The mass peak widths at $\sim 90\%$ peak height were 1.5 mamu and at 50% were 5 mamu. (3) The position of the minimum between $^{40}\text{CaH}^+$ and $^{25}\text{MgO}^+$ (or the peak of $^{40}\text{CaH}^+$) was located to within ± 0.5 mamu and the Hall voltage noted. Using the Hall voltage as control, the magnetic field was reduced by the amount determined in (2) to obtain the $^{41}\text{K}^+$ mass position and $^{41}\text{K}^+$ counted. The field was then increased to the Hall voltage corresponding to $^{40}\text{CaH}^+$ and $^{40}\text{CaH}^+$ counted and compared with previous intensities, establishing that the center of the ^{40}CaH spectral line was not displaced by magnet hysteresis or field drift. These steps appeared to show that ^{41}K as well as ^{40}CaH were properly located and the field stable to ± 1 mamu. Drift in the

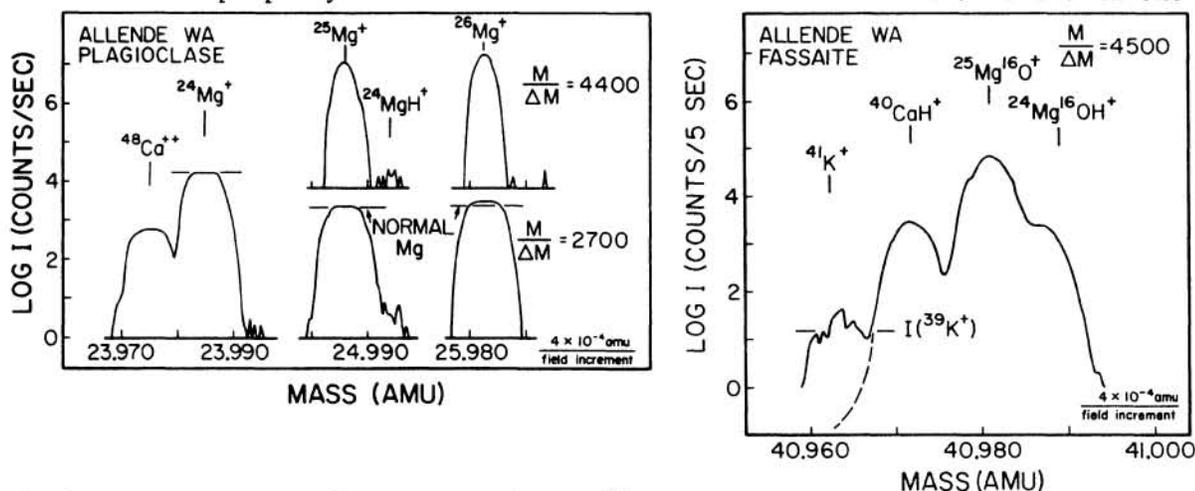


Fig.1. Mass spectra of Mg in WA plag. ^{26}Mg in WA is 22% in excess of normal. Fig.2. Mass spectrum of mass 41 in WA. $^{39}\text{K}^+ \approx ^{41}\text{K}^+$, indicating large ^{41}K excess.

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field or misplacement within this limit should result in a decrease and not increase in detected $^{41}\text{K}^+$. To identify and relocate $^{39}\text{K}^+$, $^{23}\text{NaO}^+$ at mass 39 was used when present. $^{39}\text{K}^+$ was located and the mass peak manually centered to maximize $^{39}\text{K}^+$. $^{39}\text{K}^+$ was small for pyroxene and hibonite and the exit slit was widened to a 10-100 mamu window to assure complete collection of $^{39}\text{K}^+$. Any interfering ions within this window were also collected. K isotopic measurements and K^+/Ca^+ are given in Table 1. $^{39,41}\text{K}^+$ and $^{40}\text{CaH}^+$ varied less than 30% relative to ^{42}Ca during analysis except for hibonite where variations of up to 60% were observed. Ion counts acquired on successive cycles through the mass spectrum were summed for each ion and 2σ errors calculated. Excesses of $^{41}\text{K}^+$ are clear in the measurements on two samples of WA pyroxene measured under different analytical conditions. These effects may also be seen on the spectral scan in Fig. 2. $^{39}\text{K}^+/\text{Ca}^+$ were very low and $^{41}\text{K}^+/\text{Ca}^+$ larger by an order of magnitude than normal K. From these data we tentatively conclude that there are excesses of ^{41}K in the WA inclusion. Far more intensive tests must be made to adequately demonstrate the validity of this inference. Using $\text{K}^+/\text{Ca}^+ \approx 2\text{K}/\text{Ca}$ we obtain $^{41}\text{K}^*/^{42}\text{Ca} = 1.8 \times 10^{-5}$ in one WA pyroxene and 0.9×10^{-5} in the other. The reason for the difference is not understood. $^{39}\text{K}^+/\text{Ca}^+$ is much larger for WA plagioclase, and $^{41}\text{K}^+/\text{Ca}^+$ also substantially larger than normal, but not by a large factor. $^{41}\text{K}^*/^{42}\text{Ca} = 1.4 \times 10^{-5}$ in plagioclase and appears to be a confirmation of $^{41}\text{K}^*$ effects in a mineral in which K^+ peaks are easily identified. No comparable $^{41}\text{K}^*$ is observed in mass scans on spinel from WA. Also, HAL hibonite contains no detectable $^{41}\text{K}^*$ outside of error limits.

$^{41}\text{K}^*$ in WA is not correlated with ^{39}K , Mg or Al but is correlated with Ca. $^{41}\text{K}^*/^{42}\text{Ca}$ is similar in pyroxene and plagioclase and $^{41}\text{K}^*$ is absent in spinel. From the geochemical correlation with Ca we conclude $^{41}\text{K}^*$ may plausibly be associated with the decay of short-lived ^{41}Ca . The absence of $^{41}\text{K}^*$ in hibonite is consistent with the absence of $^{26}\text{Mg}^*$. Inclusions like WA appear to have crystallized from a melt and presumably K and Ca were isotopically locally equilibrated at that time. The existence of a Mg/Al isochron is evidence for Mg isotopic equilibration [4]. Thus, ^{41}Ca must have been live in the solar nebula at the time of inclusion melting. It is less likely that $^{41}\text{K}^*$ was carried into the solar nebula in refractory grains well after the capture and decay of ^{41}Ca . An energetic particle irradiation giving a neutron fluence of $10^{17}\text{n}/\text{cm}^2$ would yield $^{41}\text{Ca}/^{40}\text{Ca} = 10^{-7}$. Other Allende inclusions have been exposed to only $\sim 10^{14}\text{n}/\text{cm}^2$, and this origin for ^{41}Ca from $^{40}\text{Ca}(n,\gamma)$ is unlikely.

The presence of live ^{41}Ca and ^{26}Al in WA requires their incorporation within a few m.y. of synthesis. The mass of material contributed by the last event is estimated at 4×10^{-4} to 2×10^{-2} of the nebular mass [6]. If the production ratio is $^{41}\text{Ca}/^{42}\text{Ca} \sim 1/2$ and the injected material is similar in composition to the solar nebula with $2 \times 10^{-4} \text{Ca} \sim 4 \times 10^{-4} \text{Ca}$ to $2 \times 10^{-2} \text{Ca}$, the interval Δ between late stage nucleosynthesis and inclusion melting is 0.4-1 m.y. An upper limit of $\Delta_{\text{max}} = 1.5$ m.y. is obtained if no nebular dilution occurred. No ^{41}Ca effects would be observed for much larger Δ .

Ref:[1]GRL 3(1976)109; [2]Nature 259(1976)549; [3]Nature 257(1975)36; [4]G.C.Acta 14(1977)1473; [5]JGR 83(1978)244; [6]Lunatic Asylum Preprint 353(1980).

Table 1.	$^{41}\text{K}^+/\text{Ca}^+$	$^{41}\text{K}^+/\text{Ca}^+ \times 10^5$	$^{25}\text{Mg}^+/\text{Ca}^+$	$^{26}\text{Mg}^+/\text{Ca}^+$	$^{41}\text{K}^+ \text{ c/s}$
WA pyrox	3.9 ± 0.4	3.6 ± 0.4	-	-	4.4
WA pyrox	1.2 ± 0.3	1.5 ± 0.3	-	-	0.38
WA plag	0.095 ± 0.005	8.1 ± 0.4	0.1264 ± 11	0.1689 ± 14	5.1
WA spinel	-	-	0.1263 ± 6	0.1388 ± 6	0.30
HAL hibonite	0.061 ± 0.013	0.9 ± 0.2	0.1241 ± 13	0.1365 ± 22	0.24
HAL hibonite	0.084 ± 0.016	0.6 ± 0.2	-	-	-
Lake Co plag	0.071 ± 0.002	$(28 \pm 1) \times 10^3$	0.1256 ± 10	0.1372 ± 11	1.4×10^4
Terrestrial	0.0742	-	0.12663	0.13981	-